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Japanese Patent

Sho 63-139364

# TONER FOR DEVELOPING ELECTROSTATICALLY CHARGED IMAGE

[Seiden Kazo Genzo Yo Tona]

Toshiki Minamidani and Hachiro Tosaka

UNITED STATES PATENT AND TRADEMARK OFFICE

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# Specification

## 1. Title of the invention

Toner for Developing Electrostatically Charged Image

## 2. Claim

A toner for developing an electrostatically charged image, characterized by the fact that at least one or more of calcium carbonate, magnesium hydroxide, silicon dioxide, aluminum silicate, aluminum hydroxide, and zirconium silicate having a particle shape with an average particle diameter of 0.1-5.0 $\mu$m and a BET specific surface of 20 $m^2/g$ or less are included in toner particles composed of a binding resin and a colorant.

## 3. Detailed explanation of the invention

(Technical field)

The present invention pertains to a toner for developing an electrostatically charged image being used in electrophotography, electrostatic printing method, etc. In

[1] Numbers in the margin indicate pagination in the foreign text.

particular, the present invention pertains to a positively chargeable toner being used in a heating roll fixing.

(Prior art)

As the electrophotography, many methods such as specification of U.S. Patent No. 2,297,691 have been known.

As developing methods for visualizing an electric latent image by a developing agent (generally, toner), for example, various methods as described in the specification of U.S. Patent No. 2,874,063, specification of U.S. Patent No. 2,618,552, specification of U.S. Patent No. 2,221,776, specification of U.S. Patent No. 3,909,258, etc., are known.

As a toner being applied to these developing methods, a fine powder in which a dye and a pigment are dispersed into a natural or synthetic resin has been used. For example, particles in which a colorant is dispersed into a binding resin such as polystyrene and finely crushed to about 1-3 $\mu$ are used as a toner. As a magnetic toner, a toner in which magnetic particles such as magnetite are included is used. In a method using a so-called binary developing agent, a toner is usually used by mixing it with carrier particles such as glass beads and iron powder.

As a method for fixing the toner image, a thermal fixing method among various known methods is practically used in terms

of various points. In particular, a contact thermal fixing /2 method using a heating roller fixer is broadly employed since its thermal efficiency is high, a heat source at a relatively low temperature can be used, and fixing can be achieved at high speed.

Then, in the contact thermal fixing method, since fixing is carried out by contacting the surface of a heating body such as heating roller to a toner and melting it, a so-called offset phenomenon in which the melted toner or semi-melted toner is attached to the surface of the heating body and transferred to following transfer papers is apt to be caused. This offset phenomenon is generated when the viscoelectricity of the toner melted by heating is inappropriate and too small.

On the other hand, when the toner is provided to developing, it is subjected to a heavy mechanical impact and compression. Its purpose is to electrify said toner, however the toner particles are crushed by these impact, etc., so that a fine powder being generated is attached to the surface of a carrier being stirred with the toner, for instance. Thereby, the characteristics as a developing agent are degraded, or the toner particles are attached to an electrostatically charged image support, causing a so-called ground stain. Thus, the formation of a good visible image is hindered.

In order to obtain a toner having a non-offset characteristic, which does not cause the above offset phenomenon, and an impact resistance for withstanding mechanical impacts such as stirring, it is effective to crosslink and polymerize a polymer as a constitutional component of said toner, and preferable durability and the storage as the toner are also simultaneously obtained.

Then, the conventional toner for developing an electrostatically charged image is manufactured by melt-kneading a soft polymer and a colorant, dispersing the colorant into the polymer, and finely crushing the colorant-dispersed polymer, however if a crosslinked polymer is used as the polymer, a large shear force must be applied during the melt-kneading. Furthermore, the effect of the crosslinked polymer being used is canceled by cutting of the molecular chains of the crosslinked polymer due to the shear force, and even if a uniform colorant-dispersed polymer is obtained, since the polymer is a crosslinked polymer, needless to say, the toner is considerably tough. Thus, it is very difficult to crush the toner into particulates with a required particle diameter (usually, in a range of 1-50 $\mu$). In other words, as mentioned above, it is difficult to manufacture the toner composed of a crosslinked polymer by the method including the melt-kneading and crushing

processes. In addition, the particle diameter distribution of the fine powder being obtained by said manufacturing method is very wide, and it must be further sent to a classifying process to obtain a toner that can be provided to practical uses. After all, there are also drawbacks of said method itself such as complicated processes and high cost.

On the other hand, as a method for directly obtaining polymer particulates without including a crushing process, there is a method that disperses and suspends a polyermizable monomer into water and suspension-polymerizes it. However, in this method, the manufacturing processes are simple, however their controls are very complicated. Also, it cannot be said that the dispersion of a charging controller and a colorant is uniform, and the toner prepared has nonuniform chargeability, which is difficult to be sufficiently provided to practical uses.

Also, a magnetic toner containing a wax and a filler such as magnesium carbonate and magnesium oxide of 5 $\mu$ or less (see Japanese Kokai Patent Application No. Sho 52[1977]-104929), a color toner containing a kaolin or calcium carbonate, a binding resin, and each colorant for yellow, magenta, and cyan (see Japanese Kokai Patent Application No. Sho 55[1980]-166652), etc., are known. However, the former is limited to a pressure

fixing toner, and the latter is limited to a color toner with a negative polarity.

(Purpose)

The present invention considers the above situation, and its purpose is to provide a toner for developing an electrostatically charged image in which the non-offset characteristic and the impact resistance of the toner are improved and the triboelectrication between toner particles or the toner and a carrier layer, the toner for developing one component and a charging member such as developing sleeve or blade is stable and which can be easily and inexpensively manufactured.

(Constitution)

The present invention is a toner for developing an electrostatically charged image characterized by the fact that at least one or more of calcium carbonate, magnesium hydroxide, silicon dioxide, aluminum silicate, aluminum hydroxide, and /3 zirconium silicate having a particle shape with an average particle diameter of 0.1-5.0 $\mu$m and a BET specific surface of 20 $m^2/g$ or less are included in toner particles composed of a binding resin and a colorant.

In other words, the above purpose is achieved by rendering an appropriate reinforcement effect through the addition of an appropriate amount of inorganic filler to the toner.

As the calcium carbonate, magnesium oxide, and magnesium hydroxide being used in the present invention, there are light, heavy, and fine particles, and in particular, fine particulates have good kneading characteristic and workability, good dispersibility into a binder resin, and good positive chargeability. Also, the silicon dioxide, aluminum silicate, aluminum hydroxide, and zirconium silicate have good negative chargeability. However, if its average particle diameter is smaller than 0.1 μm, it is difficult to be uniformly dispersed, and if a copying operation for a long time is repeated, problems such as ground fog and image density decrease are generated. Also, if the diameter is greater than 5.0 μm, the fixing characteristic of the toner is insufficient, and whitening is generated on images, so that insufficient images are formed. Therefore, its average particle diameter is preferably 0.1-5.0 μm, more preferably 0.5-3.0 μm.

Also, if the particle shape is a plate shape or an acicular shape, the reinforcement effect on the binder resin is raised, so that the fixable temperature is raised and the fixing characteristic is inferior. Also, if the particle shape is a

spherical shape, the reinforcement effect is small, and the impact resistance is insufficient. Therefore, irregular shapes are good.

Furthermore, the BET specific surface is preferably 20 $m^2/g$ or less, and if the specific surface exceeds 20 $m^2/g$, the porosity of the particles is advanced, and similarly to the spherical shape, the reinforcement effect on the binder resin is raised, so that a fixing inferiority is caused.

Also, the amount being mixed is preferably 5-70 wt% in the toner, and if the amount is less than 5 wt%, a sufficient reinforcement effect cannot be obtained. If the amount is more than 70 wt%, the fixing characteristic and the chargeability are inferior.

As the binder resin of the toner being used in the present invention, resins that have been widely used as a toner for electrophotography, for example, styrene and its substituent homopolymer such as polystyrene, poly P-chlorostyrene, and polyvinyltoluene; styrene group copolymer such as styrene-P-chlorostyrene copolymer, styrene-propylene copolymer, styrene-vinyltoluene copolymer, styrene-vinylnaphthalin copolymer, styrene-methyl acrylate copolymer, styrene-ethyl acrylate copolymer, styrene-butyl acrylate copolymer, styrene-methyl methacrylate copolymer, styrene-ethyl methacrylate copolymer,

styrene-butyl methacrylate copolymer, styrene-methyl α chloromethacrylate, styrene-acrylonitrile copolymer styrene-vinyl methyl ether copolymer, styrene-vinyl ethyl ether copolymer, styrene-vinyl methyl ketone copolymer, styrene-butadiene copolymer, styrene-isoprene copolymer, styrene-acrylonitrile-indene copolymer, styrene-maleic acid copolymer, and styrene ester maleate copolymer; polymethyl methacrylate, polybutyl methacrylate, polyvinyl chloride, polyvinyl acetate,, polyethylene, polypropylene, polyester, polyurethane, polyamide, epoxy resin, polyvinyl butyral, polyacryic acid resin, rosin, modified rosin, terpene resin, phenol resin, aliphatic or alicyclic hydrocarbon resin, aromatic petroleum resin, chlorinated paraffin, paraffin wax, etc., can be used alone or by mixing.

In the toner of the present invention, generally, the lower limit temperature of the fixing tends to rise, and for this reason, a styrene group or acrylic resin with a low glass transition temperature (35-50°C) is preferably used.

Also, in case the toner for developing an electrostatically charged image, needless to say, colorant pigments that have been used in toners are added to the above-mentioned resin components. Specifically, there are carbon black, nigrosine dye, lamp black, Sudan black SM, fast yellow G, benzidine

yellow, pigment yellow, Indian fast orange, Irugasine red, /4 paranitroaniline red, toluidine red, carmine FB, permanent bold FRR, pigment orange R, lithol red 2G, lake red C, Rhodamine FB, Rhodamine B lake, methyl violet B lake, phthalocyanine blue, pigment blue, brilliant green B, phthalocyanine green, oil yellow GG, shaddock fast yellow CGG, kaya set Y963, kaya set YG, Chinese ink blast yellow GG, shaddock fast orange RR, oil scarlet, Chinese ink blast orange G, Orasol brown B, shaddock fast scarlet CG, Eisen spiron red, BEH oil pink OP, etc.

Also, in order to use the toner of the present invention as a magnetic toner, a magnetic powder may be included. As the magnetic powder, substances that are placed in a magnetic field and magnetized are used, and there are ferromagnetic metal powders such as iron, cobalt, and nickel or alloys and compounds of magnetite, hematite, and ferrite. The content of the magnetic powder is 15-70 wt% to the toner weight.

Furthermore, if necessary, the toner of the present invention is mixed with carrier particles such as iron powder, glass beads, nickel powder, and ferrite powder and can be used as a developing agent of electric latent images.

The developing agent of the present invention can be applied to various developing methods. For example, there are magnetic brush developing method, cascade developing method,

method using an electroconductive magnetic toner described in the specification of U.S. Patent No. 3,909,258, method using a high-resistance magnetic toner described in Japanese Kokai Patent Application No. Sho 53[1978]-31136, methods described in Japanese Kokai Patent Application Nos. Sho 54[1979]-42141, Sho 55[1980]-18658, Sho 54[1979]-43027, etc., fur brush developing method, powder ground method, impression developing method, etc.

Also, in case the developing agent is held in a developing agent carrier such a sleeve, magnetic force, Coulomb force, electrostatic force, frictional force, mechanical force, etc., can be utilized.

Next, application examples are mentioned, however the present invention is not limited at all by them. Also, all parts mean parts by weight.

Application Example 1

| | |
|---|---|
| Calcium carbonate (trade name: Softon 2200 made by [illegible] Bunka Kogyo K.K., an average particle diameter of 1 $\mu$m, a BET specific surface of 5.8 $m^2/g$ | 35 parts |
| Styrene-n butyl methacrylate copolymer | 60 parts |
| Quaternary ammonium salt | 5 parts |
| C.I. pigment blue 15 | 5 parts |

A mixture with the above-mentioned composition was sufficiently stirred and mixed in a henschel mixer, heated and

melted at a temperature of 130-140°C for about 30 min by a roll mill, and cooled down to room temperature, and the kneaded product obtained was crushed and classified, so that a blue toner with a particle diameter of 5-15 μm was obtained.

3 parts of the toner was mixed with 97 parts ferrite carrier with a mesh of 100-250 coated with a silicone resin, so that a developing agent was obtained.

Next, when the above-mentioned developing agent was set in a copying machine FT-4060 of Ricoh Co., Ltd., in which an organic photosensitive body was charged at $^{e}$800 VDC, and an image was tested, a good image exhibiting a clean blue was obtained. The image was not changed even after forming 200,000 sheets of images.

Also, the amount of toner charged was measured by a blow-off method. The initial amount charged was + 16.3 μ c/g, and the amount of toner charged after running 200,000 sheets was + 15.5 μ c/g. There was little difference from the initial value.

Furthermore, the fixing characteristic was good, and winding attachment to the fixing roller and the offset phenomenon were not seen.

Comparative Example 1

Similarly to Application Example 1 except for setting calcium carbonate to an average particle diameter of 7.0 μm and

a BET specific surface of 0.8 $m^2/g$, a toner was prepared. However, the fixing characteristic was inferior, and a whitened insufficient image was formed.

Comparative Example 2

Similarly to Application Example 1 except for setting calcium carbonate to an average particle diameter of 0.05 μm and a BET specific surface of 74.2 $m^2/g$, a toner was prepared. /5 However, an insufficient image with a ground fog and a low image density of 0.86 was formed.

Application Example 2

| | |
|---|---|
| Magnesium hydroxide (trade name: Kisma 5B made by Kyowa Kagaku Kogyo K.K., an average particle diameter of 0.7 μm, a BET specific surface of 6.0 $m^2/g$ | 30 parts |
| Styrene-2-ethylhexyl acrylate copolymer | 70 parts |
| Polyethylene | 5 parts |
| C.I. pigment red 81 | 5 parts |
| C.I. pigment red 48 | 3 parts |
| Quaternary ammonium salt | 5 parts |

A mixture with the above-mentioned composition was melt-kneaded, crushed, and classified similarly to Application Example 1, so that a red toner of 5-15 μm was obtained.

100 parts of the toner was sufficiently stirred and mixed with 3 part silicon carbide (a particle diameter of 2 μm) by a speed kneader.

The toner was charged into a developing processor as shown in the figure, and when an image was tested by a continuous copying using the toner, a good image exhibiting a clean red color was obtained, and the image was not changed even after forming 50,000 sheets of images. Also, in the figure, 1 is an electrostatic latent image carrier, 2 is a toner transfer member, 3 is an elastic blade, 4 is a sponge roller, 5 is a stirring blade, 6 is a toner, and 7 is a toner tank.

This developing method is explained below. The toner 6 built in a toner tank 7 as shown in the figure is forcedly put aside to the sponge roller 4 by the stirring blade 5, and the toner is supplied to the sponge roller 4. Then, the toner introduced in the sponger roller 4 is carried to the tone transfer member 2 by the rotation of the sponge roller 4 in an arrow direction, rubbed, and electrostatically or physically adsorbed, and the toner transfer member 2 is strongly rotated in an arrow direction, and a uniform toner thin layer is formed by the elastic blade 3 made of a steel and triboelectrified. Then, the toner is carried to the surface of the electrostatically

latent image carrier 1 contacted or adjacent to the toner transfer member 2, and a latent image is developed.

An organic photosensitive body was charged at ⊖ 800 V DC, and the electrostatic latent image is exposed, so that a latent image is formed. It is developed.

Also, the fixing characteristic was good, and the winding attachment to the fixing roller and the offset phenomenon were not seen.

Comparative Example 3

Similarly to Application Example 1 except for setting magnesium hydroxide to an average particle diameter of 0.02 $\mu$m and a BET specific surface of 67.9 $m^2/g$, a toner was prepared. However, the fixing characteristic was inferior, and the offset developing was seen. A whitened insufficient image was formed.

Application Examples 3-6 and Comparative Examples 4 and 5

Toners were obtained using developing agent compositions shown in Table I by a method similar to those of Application Example 1. The image characteristic, the chargeability, and the fixing characteristic of these toner were also shown in the table.

Also, the lower limit temperature of the fixing in the fixing characteristic and the offset generation temperature were attained as follows. As for the lower limit temperature of the

fixing, using a fixer consisting of a heating roller whose surface layer was formed of Teflon and a press roller whose surface layer was formed of a silicone rubber, an operation for fixing a toner image of a sample toner transferred to a transfer paper of 84 $g/m^2$ at a rod speed of 120 mm/sec was repeated at each temperature raised stepwise from 110°C at 5°C each. The fixed image formed was rubbed with a sand erasure, and the lowest set temperature related to the fixed image exhibiting the fixed image formed was adopted as a lower limit fixing temperature. Also, the fixer used here has no a silicone oil feed mechanism.

Also, in the measurement of the offset generation temperature, according to the measurement of the lower limit fixing temperature, the toner image was transferred and fixed by the above-mentioned fixer, and a white transfer paper was sent to the fixer under similar conditions. Then, an operation for observing whether not a toner stain was generated was repeated in a state in which the set temperature of the heating roller of the above-mentioned fixer was sequentially raised, and the offset generation temperature was attained.

Table I /6

| 現像剤の組成 | | 画像性 | | 帯電特性 (μc/g) | | 定着特性 | |
|---|---|---|---|---|---|---|---|
| | | 初期 | 20万枚目 | 初期 | 20万枚目 | 定着下限温度 | オフセット発生温度 |
| 実施例3 | 酸化マグネシウム（平均粒径 2μm BET比表面積12.3 m²/g） 20部<br>不飽和ポリエステル樹脂 77部<br>ポリプロピレン 3部<br>カーボンブラック 10部<br>ニグロシン染料 0.5部 | 地かぶり全くなし。画像濃度（1Dと再すと1.48 | 同左<br>〃<br>1.55 | +18.2 | +17.4 | 155℃ | 240℃以上 |
| 実施例4 | 炭酸マグネシウム（平均粒径 2μm BET比表面積 3.3m²/g） 50部<br>スチレン－ブチルアクリレート共重合体 50部<br>ポリエチレン 5部<br>カーボンブラック 10部<br>ニグロシン染料 2部 | 地かぶり全くなし。1D－1.50 | 同左<br>1D<br>－<br>1.52 | +20.5 | +18.8 | 160℃ | 240℃以上 |
| 実施例5 | 炭酸カルシウム（平均粒径 0.8μm BET 比表面積10.3 m²/g） 20部<br>スチレン－ブチルアクリレート共重合体 80部<br>C.I.ピグメントブルー15 5部<br>4級アンモニウム塩 5部 | 地かぶりなし。青色鮮明 | 同左 | +14.6 | +15.6 | 155℃ | 240℃ |

1. Composition of developing agent
2. Image characteristic
3. Charging characteristic (μc/g)
4. Fixing characteristic
5. Initial
6. After 200,000 sheets
7. Initial
8. After 200,000 sheets
9. Lower limit fixing temperature
10. Offset generation temperature
11. Application Example 3
12. Application Example 4
13. Application Example 5

14. Magnesium oxide (an average particle diameter of 2 μm and a BET specific surface of 2.3 $m^2/g$) 20 parts
Unsaturated polyester resin 77 parts
Polypropylene 3 parts
Carbon black 10 parts
Nigrosine dye 0.5 part

15. Magnesium carbonate (an average particle diameter of 2 μm and a BET specific surface of 3.3 $m^2/g$) 50 parts
Styrene-n butyl acrylate copolymer 50 parts
Polypropylene 5 parts
Carbon black 10 parts
Nigrosine dye 2 parts

16. Calcium carbonate (an average particle diameter of 0.8 μm and a BET specific surface of 0.3 $m^2/g$) 20 parts
Styrene-n butyl acrylate copolymer 50 parts
C.I. pigment blue 15 5 parts
Quaternary ammonium salt 5 parts

17. No ground fog, image density (called ID) 1.48

18. Same as left

19. 240°C or higher

20. No ground fog, ID 1.50

21. Same as left

22. 240°C or higher

23. No ground fog, blue sharp

24. Same as left

Table I (continued)

| 現像剤の組成 | | 画像性 | | 帯電特性 (μc/g) | | 定着特性 | |
|---|---|---|---|---|---|---|---|
| | | 初期 | 20万枚目 | 初期 | 20万枚目 | 定着下限温度 | オフセット発生温度 |
| 実施例8 | 水酸化マグネシウム（平均粒径0.5 μm、BET比表面積17.2 m²/g）15部<br>スチレン−2エチルヘキシルアクリレート共重合体 45部<br>C.I.ディスパーズイエロー33 5部<br>P-スチリルジブチルホスフィン共重合体 10部 | 地かぶりなし。<br>黄色鮮明 | 同左 | -15.6 | -17.2 | 150℃ | 240℃以上 |
| 比較例4 | 前記マグネシウムの配合量を100部樹脂分を30部とすることを除いて、実施例3と同じ組成のトナー。 | 地かぶりあり ID−1.01 | 同左 ID−0.82 | -10.2 | -6.3 | 200℃ | 140℃以上 |
| 比較例5 | 前記マグネシウムの配合量を5部、樹脂分を100部とすることを除いて実施例4と同じ。 | 地かぶりなし。 ID−1.36 | 地かぶりあり ID−1.41 | -22.2 | -20.5 | 150℃ | 200℃ |

1. Composition of developing agent

2. Image characteristic

3. Charging characteristic (μc/g)

4. Fixing characteristic

5. Initial

6. After 200,000 sheets

7. Initial

8. After 200,000 sheets

9. Lower limit fixing temperature

10. Offset generation temperature

11. Application Example 6

12. Comparative Example 4

13. Comparative Example 5

14. Magnesium hydroxide (an average particle diameter of 0.5 μm and a BET specific surface of 17.2 $m^2/g$) 15 parts
Styrene-2 ethylhexyl acrylate copolymer 45 parts
C.I. disperse yellow 33 5 parts
P-styryldibutylphosphine copolymer 10 parts

15. Toner with the same composition as that of Application Example 3 except for setting the amount of magnesium oxide being mixed to 100 parts and the resin portion to 30 parts

17. Same composition as Application Example 4 except for setting the amount of magnesium carbonate being mixed to 5 parts and the resin portion to 100 parts

18. No ground fog, yellow sharp

19. Same as left

20. 240°C or higher

21. Existence of ground fog, ID 1.01

22. Same as left

23. 140°C or higher

24. No ground fog, ID 1.36

25. Existence of ground fog, ID 1.44

Application Example 7

Styrene-n butyl acrylate copolymer (a weight average molecular weight of 270,000 and a glass transition point of 46°C) 40 parts

Styrene-2 ethylhexyl-n butyl acrylate copolymer (a weight average molecular weight of 280,000 and a glass transition point of 60°C) 30 parts

Calcium carbonate (an average particle diameter of 1 μm and a BET specific surface of 5.8 $m^2/g$) 30 parts

Nigrosine 1 part

Carbon black 10 parts

The above components were well mixed, heated and melted at a temperature of 130-140°C for about 45 min by a roll mill, and cooled down to room temperature, and the kneaded product obtained was crushed and classified, so that a black toner with a particle diameter of 5-20 μm was obtained.

3 parts of the toner was mixed with 97 parts ferrite carrier with a mesh of 100-250 coated with a silicone resin, so

that a developing agent was obtained. The above-mentioned developing agent was set in a copying machine FT-4060 of our company in which an organic photosensitive body was charged at ⊖ 800 V DC, and copying was tested. Also, the lower limit fixing temperature and the offset generation temperature were evaluated. As a result, the fixing was carried out at a very high temperature of 120°C, and no offset was generated up to 240°C. Also, the image was not changed but was sharp, even after forming 200,000 sheets of images. Also, when the amount of toner charged was measured by the blow-off method. The initial amount charged was + 18.0 $\mu$ c/g, and the amount of toner charged after running 200,000 sheets was + 16.2 $\mu$ c/g. There was little difference from the initial value.

Application Example 8

| | |
|---|---|
| Styrene-n butyl methacrylate (a weight average molecular weight of 120,000 and a glass transition point of 43°C) | 30 parts |
| Polyester resin (a number average molecular weight of 2,500 and a glass transition point of 55°C) | 50 parts |
| Magnesium hydroxide (an average particle diameter of 0.7 $\mu$m and a BET specific surface of 6.0 $m^2/g$) | 20 parts |
| Quaternary ammonium salt | 5 parts |
| C.I. pigment red 81 | 5 parts |

C.I. pigment red 48 3 parts

The above components were well mixed, melted, kneaded, crushed, and classified similarly to Application Example 7, so that a red toner of 5-15 μm was obtained.

100 parts of the toner was mixed with 3 parts silicon carbide (a particle diameter of 2 μm) and 0.1 part colloidal silica by a speed kneader and sufficiently stirred, so that a /7 developing agent was obtained.

The toner was charged into a developing processor as shown in the figure, a continuous copying was carried out similarly to Application Example 2, and an image was tested. As a result, a good image exhibiting a sharp red color was obtained, and the image was not changed even after forming 50,000 sheets of images. In this case, an organic photosensitive body was charged at ⊖ 800 V DC, and the electrostatic latent image was exposed, so that a latent image was formed. It was developed.

When its fixing characteristic was evaluated, it was fixed at a low temperature of 125°C, and no offset was generated up to 220°C.

Application Examples 9-14

Using developing agent compositions shown in Table II, toners were obtained by a method similar to that of Application Example 7. When the image characteristic, the chargeability,

and the fixing characteristic of these toners were measured, the results as shown in Table II were obtained. Also, in Table II, since Application Examples 9, 10, 12, and 13 were toners with a negative polarity, a Se photosensitive body was used in a copying test and charged at ⊖ 750 V DC.

Table II

| 現像剤の組成 | | 画像性 | | 帯電特性 (μc/g) | | 定着特性 (℃) | |
|---|---|---|---|---|---|---|---|
| | | 初期 | 20万枚目 | 初期 | 20万枚目 | 定着下限温度 | オフセット発生温度 |
| 実施例9 | スチレン-エチルアクリレート-メチルアクリレート共重合体（重量平均分子量80,000ガラス転移点56℃）100部、不飽和ポリエステル 60部 ケイ酸アルミニウム（平均粒径1.5μm、BET比表面積2.2m²/g） 10部 含クロムモノアゾ染料 1部 カーボンブラック 7部 | 地かぶり全く画像濃度（以下1.0とあす） 1.45 | 同左 〃 1.50 | -15.0 | -13.2 | 130℃ | 220℃ |
| 実施例10 | メチルアクリレート-シクロヘキシルアクリレート共重合体（重量平均分子量80,000, ガラス転移点35℃） 20部 二酸化ケイ素（平均粒径4.0μm、BET比表面積18.0 m²/g） 7部 エポキシ樹脂 7部 含クロムモノアゾ染料 0.5部 カーボンブラック 10部 | 地かぶり全くなし 10 −1.35 | 同左 10− 1.40 | -20.1 | -18.6 | 140℃ | 240℃ |

1. Composition of developing agent
2. Image characteristic
3. Charging characteristic (μc/g)
4. Fixing characteristic
5. Initial
6. After 200,000 sheets
7. Initial
8. After 200,000 sheets

9. Lower limit fixing temperature

10. Offset generation temperature

11. Application Example 9

12. Application Example 10

13. Styrene-ethyl acrylate-methyl acrylate copolymer (a weight average molecular weight of 10,000 and a glass transition temperature of 36°C) 10 parts

    Unsaturated polyester 80 parts

    Aluminum silicate (an average particle diameter of 1.5 μm and a BET specific surface of 2.2 $m^2/g$) 10 parts

    Monoazo dye containing chromium 1 part

    Carbon black 7 parts

14. Methyl acrylate-cyclohexyl acrylate copolymer (a weight average molecular weight of 80,000 and a glass transition temperature of 36°C) 20 parts

    Silicon dioxide (an average particle diameter of 4.0 μm and a BET specific surface of 10.0 $m^2/g$) 7 parts

    Epoxy resin 73 parts

    Monoazo dye containing chromium 0.5 part

    Carbon black 10 parts

15. No ground fog, image density (called ID) 1.45

16. Same as left

17. No ground fog, ID 1.36

18. Same as left

Table II (continued)

表2のつづき

| 現像剤の組成 | | 画像性 | | 帯電特性 (μc/g) | | 定着特性 (℃) | |
|---|---|---|---|---|---|---|---|
| | | 初期 | 20万枚目 | 初期 | 20万枚目 | 定着下限温度 | オフセット発生温度 |
| 実施例11 | スチレン－nブチルアクリレート共重合体（重量平均分子量270,000, ガラス転移点65℃） 20部<br>スチレン－2エチルヘキシル－nブチルアクリレート共重合体（実施例7のもの） 20部<br>酸化マグネシウム 60部<br>ポリプロピレン 5部<br>カーボンブラック 10部<br>ニグロシン染料 2部 | 地かぶり全くなし<br>10<br>－1.41 | 同左<br>10－<br>1.36 | －15.6 | －17.5 | 140℃ | 240℃以上 |
| 実施例12 | ケイ酸アルミニウムをケイ酸ジルコニウム（平均粒径 0.5μm, BET比表面積6.5m²/g）にすることを除いて実施例9と同じ組成のトナー | 地かぶり全くなし<br>10-1.29 | 同左<br>10－<br>1.45 | －22.3 | －16.8 | 135℃ | 220℃ |
| 実施例13 | 二酸化ケイ素を水酸化アルミニウム（平均粒径 0.6μm, BET比表面積6.5m²）にすることを除いて実施例10と同じ組成のトナー | 地かぶり全くなし<br>10-1.43 | 同左<br>10－<br>1.49 | －15.2 | －13.9 | 130℃ | 235℃ |
| 実施例14 | 酸化ケイ素 平均粒径 0.8μm<br>BET比表面積 10.3m/g 50部<br>スチレン－nブチルメタアクリレート（実施例8のもの） 50部<br>ニグロシン染料 2.5部<br>カーボンブラック 10部 | 地かぶり全くなし<br>10<br>－1.30 | 同左<br>10－<br>1.40 | －17.2 | －18.5 | 145℃ | 220℃ |

1. Composition of developing agent

2. Image characteristic

3. Charging characteristic (μc/g)

4. Fixing characteristic

5. Initial

6. After 200,000 sheets

7. Initial

8. After 200,000 sheets

9. Lower limit fixing temperature

10. Offset generation temperature

11. Application Example 11

12. Application Example 12

13. Application Example 13

14. Application Example 14

15. Styrene-n butyl acrylate copolymer (a weight average molecular weight of 270,000 and a glass transition temperature of 46°C) 20 parts

    Styrene-2 ethylhexyl-n butyl acrylate copolymer (Application Example 7) 20 parts

    Magnesium oxide 50 parts

    Polypropylene 5 parts

    Carbon black 10 parts

    Nigrosine dye 2 parts

16. Toner with the same composition as that of Application Example 9 except for changing the aluminum silicate to zirconium silicate (an average particle diameter of 0.5 $\mu$m and a BET specific surface of 0.5 $m^2/g$)

17. Toner with the same composition as that of Application Example 10 except for changing the silicon dioxide to

aluminum hydroxide (an average particle diameter of 0.6 μm and a BET specific surface of 6.5 $m^2/g$)

18. Calcium carbonate (an average particle diameter of 0.8 μm and a BET specific surface of 10.3 $m^2/g$) 50 parts
    Styrene-n butyl methacrylate (Application Example 8) 50 parts
    Nigrosine dye 2.5 parts
    Carbon black 10 parts
19. No ground fog, ID 1.41
20. Same as left
21. 240°C or higher
22. No ground fog, ID 1.29
23. Same as left
24. No ground fog, ID 1.43
25. Same as left
26. No ground fog, ID 1.30
27. Same as left

(Effects)

According to the present invention, the following effects are obtained.

(1) In fixing by a heating roller, the non-offset characteristic is improved by an appropriate reinforcement effect.

(2) The impact resistance is improved.

(3) Even after a continuous copying, an image with a quality equivalent to the initial image is obtained.

(4) The triboelectrification with a positive polarity is stably obtained.

(5) There are no strong attachment of the toner to photosensitive body, developing sleeve, blade, etc., filming, and fusion.

(6) A good storage stability is exhibited.

(7) Economical

(8) A sharp color image can be maintained.

## 4. Brief description of the figure

The figure is an illustrative diagram showing a developing processor used in testing of the toner of the present invention.

1 Electrostatic latent image carrier

2 Toner transfer member

3 Elastic blade

4 Sponge roller

5 Stirring blade

6 Toner

7 Toner tank